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**DE FR GB**(71) Applicant: **YAZAKI CORPORATION**  
**4-28, Mita 1-chome**  
**Minato-ku Tokyo 108(JP)**Applicant: **MITSUBISHI CORPORATION**  
**6-3, Marunouchi 2-chome**  
**Chiyoda-ku Tokyo 100(JP)**(72) Inventor: **Endo, Morinobu**  
**615, Kitaharacho**  
**Suzaka-shi, Nagano 382(JP)**  
Inventor: **Ohashi, Yoshio**  
**4107-9, Yaho**  
**Kunitachi-shi, Tokyo 186(JP)**  
Inventor: **Katsumata, Makoto**  
**Yazaki Parts Co.,Ltd. 252, Kawashimada**  
**Gotenba-shi, Shizuoka 412(JP)**  
Inventor: **Yamanashi, Hidenori**  
**Yazaki Parts Co.,Ltd. 252, Kawashimada**  
**Gotenba-shi, Shizuoka 412(JP)**(74) Representative: **Patentanwälte Grünecker,**  
**Kinkeldey, Stockmair & Partner**  
**Maximilianstrasse 58**  
**W-8000 München 22(DE)**(54) **Fluorinated graphite fibers and method of manufacturing them.**

(57) Fluorinated graphite fibers comprising an intercalated compound of graphite fibers having a three-dimensional crystal structure in which carbon hexagonal network faces are substantially in parallel with the axis of fibers and oriented in a coaxial manner and fluorine, wherein the length of repeating periods in the direction of C-axis of the crystals coexist within a range from 5 to 24 Å. The fluorinated carbon fibers are manufactured by graphitizing gas phase-grown carbon fibers obtained by thermally decomposing a hydrocarbon compound in a non-oxidative atmosphere under the presence of a catalyst supported on a substrate or bringing ultra-fine metal particles catalyst suspended in a high temperature zone into contact with a hydrocarbon compound, thereby obtaining graphite fibers having a three-dimensional crystal structure in which the carbon hexagonal network faces are substantially in parallel with the axis of fibers and oriented in a coaxial manner and then bringing them into contact with fluorine.

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## FLUORINATED GRAPHITE FIBERS AND METHOD OF MANUFACTURING THEM

## BACKGROUND OF THE INVENTION

## Field of the Invention

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The present invention concerns carbon fibers suitable to the use in electroconductive composite materials, etc.

## 10 Description of the Prior Art

Since carbon fibers are light in weight and excellent in mechanical strength, as well as have satisfactory electroconductivity, they have been utilized in various application fields of use as composite materials in combination with metals, plastics or carbon materials.

15 By the way, since the electroconductivity of the carbon material is poor as compared with that of metal material, improvement for the conductivity of the carbon material has now been put under study, and it has been known to introduce various kinds of molecules, atoms or ions, for example, nitric acid between the layers of graphite crystals thereby obtaining an inter-metallic compound with improved conductivity. Further, while it has been considered that the intercalated compound of a covalent bond type obtained by reacting  
20 graphite and fluorine exhibits insulative property, it has also been known that an electroconductive intercalated compound can be obtained by reacting flaky or powdery graphite such as natural graphite or artificial graphite and fluorine. However, since such an intercalated compound is powdery, it involves a problem that homogenous and stabilized conductivity cannot be obtained with ease and the strength is reduced when the compound is formulated into a composite material.

25 On the other hand, pitch type graphite fibers or PAN type graphite fibers show not so developed crystal structure, excellent electroconductivity cannot be obtained for the intercalated compound and, in addition, it is difficult to attain uniform dispersion in the composite material. Furthermore, there has also been known of using graphite fibers obtained by graphitizing gas phase grown carbon fibers having more complete crystal structure and reacting them, for example, with nitric acid, metal chlorine or bromine, but they involve  
30 drawback that the stability is poor to increase electric resistance with lapse of time and they bring about corrosion to the apparatus in contact therewith due to decomposition products.

## OBJECT OF THE INVENTION

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In view of the above, the object of the present invention is to provide graphite intercalated compound fibers which are remarkably excellent in the stability in air or heat stability, show satisfactory conductivity and can be blended easily with thermoplastic resins, etc., as well as are suitable to be used as electroconductive composite material.

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## SUMMARY OF THE INVENTION

45 comprising an intercalated compound of graphite and fluorine, wherein carbon hexagonal network faces are substantially in parallel with the axis of fibers and oriented in a coaxial manner and fluorine, wherein lengths of the repeating periods in the direction of C-axis of the crystals being present coexist within a range from 5 to 24 Å.

50 The fluorinated graphite fibers according to the present invention can be manufactured by a method comprising graphitizing the gas phase-grown carbon fiber obtained by thermally decomposing a hydrocarbon compound in a non-oxidative atmosphere under the presence of a catalyst supported on a substrate thereby obtaining graphite fibers having a three-dimensional crystal structure in which the carbon hexagonal network faces are substantially in parallel with the axis of fibers and oriented in a coaxial manner and then bringing them into contact with fluorine.

In addition, they can be manufactured also by the method of graphitizing gas phase-grown carbon

fibers obtained by bringing ultra-fine metal particle catalyst suspended in a high temperature zone into contact with a hydrocarbon compound thereby obtaining graphite fibers having a three-dimensional crystal structure in which carbon hexagonal network faces are substantially in parallel with the axis of fibers and oriented in a coaxial manner and then bringing them into contact with fluorine.

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#### DETAILED DESCRIPTION OF THE INVENTION

The carbon fibers as the material for the fluorinated graphite fibers according to the present invention are obtained by using a hydrocarbon compound, for example, aromatic hydrocarbon such as toluene, benzene or naphthalene and aliphatic hydrocarbon such as propane, ethane or ethylene, preferably, benzene or naphthalene as the starting material, gasifying the above-mentioned starting material, bringing the same together with a carrier gas such as hydrogen in contact with a catalyst comprising super-fine metal particles, for example, iron, nickel, iron-nickel alloy, etc. with a grain size of 100 to 300 Å in a reaction zone at 900 - 1500 °C and decomposing them.

The thus obtained carbon fibers are applied with a heat treatment at a temperature of from 1500 to 3500 °C, preferably, 2500 to 3000 °C, for 3 to 120 min, preferably, 30 to 60 min in an inert gas atmosphere such as argon and formed into graphite fibers having a three dimensional crystal structure in which carbon hexagonal network faces are substantially in parallel with the axis of fibers and oriented in a coaxial manner. In this case, if the heat treatment temperature is lower than 1500 °C, the crystal structure of carbon does not develop sufficiently. On the other hand, if the temperature exceeds 3500 °C, the effect is not enhanced particularly and it is not economical. Further, if the heating treating time is shorter than 10 min, the effect of the heat treatment is not sufficient to cause great deviation in the degree of the development of the crystal structure. On the other hand, if it exceeds 120 min, no further improvement can be recognized.

The thus obtained carbon fibers may be applied with a purification treatment if necessary before or after the heat treatment for the graphitization, or they may be pulverized by using a ball mill, rotor speed mill, cutting mill or like other appropriate pulverizer. Although such pulverization is not essential, it is preferred since the easiness in forming the intercalated compound or dispersibility upon compositing with other material can be improved.

For fluorinating the thus obtained graphite fibers, there may be used a method of contacting them with a fluorine gas at a pressure not less than 100 Torr, preferably, from 300 to 1500 Torr at a temperature lower than 200 °C, preferably, from -10 to +120 °C for more than 10 min, preferably, from 48 to 72 hours. In this case, for promoting the fluorination, a catalyst such as silver fluoride may be used.

In the course of the fluorination, if the temperature of contact between the graphite fibers and the fluorine gas exceeds 200 °C, fluorinated graphite of a covalent bond type is formed, failing to obtain fibers of excellent electroconductivity. Further, it is necessary that the pressure of the fluorine gas is at least 100 Torr and, if it is less than that, aimed fluorinated intercalated compound cannot be obtained. Further, more than 10 minutes of time of contact between graphite fibers and fluorine is necessary and it is suitably 40 hours or longer, for example, under normal temperature and pressure although varying depending on the reaction temperature and the pressure. However, longer reaction time is not desired, since the crystal structure deviates from the aimed range which, as a result, lowers the electroconductivity.

Under the application of the manufacturing conditions as described above, the fluorinated graphite fibers thus obtained have a composition of  $C_5F$  -  $C_{30}F$ , and the length  $l_c$  for the repeating period in the direction of the C-axis of the crystals is from 5 to 24 Å.

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#### (Example 1)

A catalyst obtained by coating a liquid prepared by dispersing particles of a metal iron catalyst with the grain size of less than 300 Å into alcohol on a mullite ceramic sheet was dispensed and deposit on a substrate, which was placed in a horizontal tubular electric furnace. Then, a gas mixture of benzene and hydrogen was introduced while controlling the temperature to 1000 - 1100 °C to cause catalytic decomposition, thereby obtaining carbon fibers with 2 to 30 mm length and 5 to 50 μm diameter.

Then, the carbon fibers were placed in an electric furnace and graphitized by being held in an argon atmosphere at 2950 - 3000 °C for 30 min. It was confirmed by X-ray diffraction device and an electron microscope, that the thus obtained graphite fibers X had a 3-dimensional crystal structure in which carbon hexagonal network faces were in parallel with the axis of fibers and oriented in a coaxial manner and the lattice constant  $d_{002}$  was 3.36 Å and the crystal size  $l_c$  in the C-axis direction (002) was greater than 1000

Å.

One gram of the thus obtained graphite fibers and about 1 mg of a powdery silver fluoride were moderately mixed and charged in a nickel boat in a tubular reactor made of nickel. After evacuating the inside sufficiently, a fluorine gas at high purity was introduced at a room temperature and they were reacted for 72 hours while keeping the pressure at 760 Torr. Subsequently, fluorine was introduced into and adsorbed on an alumina-packed adsorption column while introducing argon into the tubular reactor and replacing the gas at the inside, to recover fluorinated graphite fibers A.

When the thus obtained fluorinated graphite fibers A were subjected to elemental analysis, it was found that the fibers had a composition of  $C_{8.3}F$ . Further, when the repeating period length  $l_c$  in the C-axis direction of the crystals was measured by X-ray diffractometry, values at 9.42 Å and at 12.6 Å were obtained to find that the product was a mixture of intercalated compounds with the stage numbers of 2 and 3.

Then, the electric resistance of the fluorinated graphite fibers A was measured by a DC 4-Point-Probe method and, further, the electric resistance was measured again after leaving for three months in atmospheric air to examine the stability. In addition, high temperature stability was also examined by measuring the electric resistance 30 min and 3 hours after maintaining them at 250°C.

The results of the measurement are shown in Table 1 in comparison with the results of measurement for not-treated graphite fibers X.

Table 1

Specimen	Electric Resistivity (u ohm.cm)			
	Stability at normal temperature		Stability at high temperature *	
	Just after production	After 3 months	30 min after	3 hr after
A	4.5	no change	4.6	5.0
X	60		60	

\* : allowed to stand at 250°C

(Example 2)

While flowing hydrogen from below a vertical tubular electric furnace controlled to a temperature of 1000 to 1100°C, particles of a metal iron catalyst with the grain size of about 300 Å were suspended, to which a gas mixture of benzene and hydrogen was introduced from below and subjected to catalytic decomposition, to obtain graphite fibers of 0.01 - 1 mm length and 0.1 - 0.5 µm diameter. Then, the carbon fibers were pulverized by using a planetary ball mill (P-5 type, manufactured by Fliche Japan Co.) at a number of rotation of 500 rpm for 20 min.

The pulverized carbon fibers were charged in an electric furnace and graphitized while being held in an argon atmosphere at 2960 - 3000°C for 30 min. It was confirmed from X-ray diffraction device and electron

was from 3.37 to 3.40 Å and the crystal size in the C-axis direction  $l_c(002)$  was 0.4-1.0 µm (and they were excellent graphite fibers).

The thus obtained graphite fibers Y were fluorinated in the same procedures as those in Example 1 to recover fluorinated graphite fibers B.

When the resultant fluorinated graphite fibers B were subjected to elementary analysis, it was found that they had a composition of  $C_{8.3}F$ . Further, when the repeating period length  $l_c$  in the C-axis direction of the crystals was measured by X-ray diffractometry, values at 9.42 Å and at 12.6 Å were obtained to find that the product was a mixture of intercalated compounds with the number of stages 2 and 3.

One gram of the powder such fluorinated graphite fibers was placed in a cylinder of 1 cm diameter made of insulative material which was put vertically between upper and lower brass electrodes. Then, the

electric resistance between the upper and the lower electrodes was measured while compressing at a pressure up to 2 t/cm<sup>2</sup> to determine the volumic resistivity at a packing density of 1.6 g/cm<sup>3</sup>. Further, the electric resistance was again measured after leaving them in atmospheric air for three months to examine the stability. Furthermore, high temperature stability was also examined by measuring the electric resistance 30 min and 3 hrs after at 250 °C.

The results of measurement are shown in Table 2 in comparison with the results of the measurements for not-treated graphite fibers Y.

#### 10 (Example 3)

Particles of a metal iron catalyst with the grain size of about 100 Å were suspended in a vertical tubular electric furnace controlled to a temperature of 1000 to 1100 °C, to which a gas mixture of benzene, hydrogen, carbon monoxide and carbon dioxide was introduced from below to take place catalytic combustion, thereby obtaining carbon fibers of 0.01 to 3 mm length and 1 to 5 μm diameter. Then, the carbon fibers were pulverized in the same manner as in Example 2 and then graphitized to obtain graphite fibers Z, which were further fluorinated to obtain a powder of fluorinated graphite fibers C.

The composition and the crystal structure of the powder of the fluorinated graphite fibers C were quite identical with those of the fluorinated graphite fibers B obtained in Example 2.

Further, for the powder of the fluorinated graphite fibers C, the volumic resistivity was measured and, further, stability in the atmospheric air and stability at high temperature were also examined like those in Example 2.

The results of the measurement are shown in Table 2 in comparison with the results of measurement for not-treated graphite fibers Z.

Table 2

Specimen	Electric Resistivity (10 <sup>-3</sup> ohm.cm)			
	Stability at normal temperature		Stability at high temperature *	
	Just after production	After 3 months	30 min after	3 hr after
B	4.5	no change	4.5	5.5
C	2.2	no change	2.3	2.8
Y	20		20	
Z	10		10	

\* : allowed to stand at 250 °C

#### 45 (Example 4)

Fluorinated graphite fibers D were obtained using the graphite fibers X obtained by the same procedures as those in Example 1 and by conducting fluorination by the same procedures as those in Example 1 except for reacting for 48 hours while keeping the pressure of fluorine at 700 Torr.

When the thus obtained fluorinated graphite fibers D were subjected to elemental analysis, it was found that the fibers had a composition of C<sub>20.2</sub>F. Further, when the repeating period length lc in the C-axis direction of the crystals was measured by X-ray diffractometry, values at 16.42 Å and at 19.80 Å were obtained to find that the product was a mixture of intercalated compounds with the stage number of 4 and 5.

Then, the electric resistance of the fluorinated graphite fibers D was measured by the same DC 4-Point-Probe method as in Example 1.

The results of the measurement are shown in Table 3 in comparison with the results of measurement for the fluorinated graphite fibers A and not-treated graphite fibers X.

## (Comparative Example 1)

Fluorinated graphite fibers E were obtained using the graphite fibers X obtained by the same procedures as those in Example 1 and by conducting fluorination by the same procedures as those in Example 1 except for reacting for 24 hours while keeping the pressure of fluorine at 760 Torr.

When the thus obtained fluorinated graphite fibers E were subjected to elemental analysis, it was found that the fibers had a composition of  $C_{40.3}F$ . Further, when the repeating period length  $l_c$  in the C-axis direction of the crystals was measured by X-ray diffractometry, the structure of the graphite fibers X remained definitely and the formation of the intercalated compound having the periodical structure could not be confirmed.

Then, the electric resistance of the fluorinated graphite fibers A was measured by the same DC 4-Point-Probe method as in Example 1 and the results are shown together in Table 3.

## 15 (Example 5)

Fluorinated graphite fibers F were obtained using the graphite fibers X obtained by the same procedures as those in Example 1 and by conducting fluorination by the same procedures as those in Example 1 except for reacting for 144 hours while keeping the pressure of fluorine at 760 Torr.

When the thus obtained fluorinated graphite fibers F were subjected to elemental analysis, it was found that the fibers had a composition of  $C_{5.7}F$ . Further, when the repeating period length  $l_c$  in the C-axis direction of the crystals was measured by X-ray diffractometry, values at 5.14 Å which was extremely intense and at 9.38 Å which was extremely weak were obtained to find that most of the intercalated compound had a stage number of 1, being mixed with a small amount of stage number of 2.

Then, the electric resistance of the fluorinated graphite fibers F was measured by the same DC 4-Point-Probe method as in Example 1 and the results are shown together in Table 3.

Table 3

Specimen	Electric resistivity ( $\mu$ cm)
A	4.5
D	5.3
E*	45
F	8
X*	60

\* : Comparative Example

## 45 (Example 6)

Fluorinated graphite fibers G were obtained using the graphite fibers Y obtained by the same

## Example 4.

When the thus obtained fluorinated graphite fibers G were subjected to elemental analysis, it was found that the fibers had a composition of  $C_{22.5}F$ . Further, when the repeating period length  $l_c$  in the C-axis direction of the crystals was measured by X-ray diffractometry, values at 13.6, 17.1 and 20.8 Å were obtained to find that the product was a mixture of intercalated compounds with the stage number of 3, 4 and 5.

The electric resistance of the fluorinated graphite fibers G was measured by the same powder method as in Example 2 and the volumic resistivity at a packing density of 1.6 g/cm<sup>3</sup> was shown in Table 4 in comparison with the results of the measurement for the fluorinated graphite fibers B and not-treated graphite fibers A.

## (Example 7)

Fluorinated graphite fibers H were obtained using the graphite fibers Y obtained by the same procedures as those in Example 2 and by conducting fluorination by the same procedures as those in Example 5.

When the thus obtained fluorinated graphite fibers F were subjected to elemental analysis, it was found that the fibers had a composition of  $C_{8.3}F$ . Further, when the repeating period length  $l_c$  in the C-axis direction of the crystals was measured by X-ray diffractometry, a weak peak at 5.17 Å and strong peaks at 9.41 and 12.78 Å were obtained to find that most of the intercalated compound had a stage number of 2 and 3, being mixed with a small amount of stage number of 1.

The electric resistance of the fluorinated graphite fibers H was measured by the same powder method as in Example 2 and the results are shown together in Table 4.

## (Example 8)

Fluorinated graphite fibers I were obtained using the graphite fibers Z obtained by the same procedures as those in Example 3 and by conducting fluorination by the same procedures as those in Example 4.

When the thus obtained fluorinated graphite fibers I were subjected to elemental analysis, it was found that the fibers had a composition of  $C_{19.8}F$ . Further, when the repeating period length  $l_c$  in the C-axis direction of the crystals was measured by X-ray diffractometry, values at 16.4 Å and at 19.8 Å were obtained to find that the product was a mixture of intercalated compounds with the stage number of 4 and 5.

Then, the electric resistance of the fluorinated graphite fibers I was measured by the same powder method as in Example 2 and the results are shown in Table 4 in comparison with the results of measurement for the fluorinated graphite fibers C and not-treated graphite fibers Z.

Table 4

Specimen	Electric resistivity ( $10^{-3}$ cm)
B	4.5
G	4.9
H	4.9
Y*	20
C	2.2
I	2.4
X*	10

\* : Comparative Example

The fluorinated graphite fibers according to the present invention have a reduced weight than metal and higher electroconductivity than conventional carbon materials, as well as they keep higher stability as compared with conventional graphite intercalated compounds. In addition, they show satisfactory dispersibility, for example, to synthetic resins, can effectively provide electroconductivity even with a small amount and, thus, are suitable for use in composite materials, etc.

## Claims

(1) Fluorinated graphite fibers comprising an intercalated compound of graphite fibers having a three-dimensional crystal structure in which carbon hexagonal network faces are substantially in parallel with the axis of fibers and oriented in a coaxial manner and fluorine, wherein the length of repeating periods in the direction of C-axis of the crystals coexist within a range from 5 to 24 Å.

(2) A method of manufacturing fluorinated carbon fibers as defined in claim 1, wherein the method

comprises graphitizing gas phase-grown carbon fibers obtained by thermally decomposing a hydrocarbon compound in a non-oxidative atmosphere under the presence of a catalyst supported on a substrate thereby obtaining graphite fibers having a three-dimensional crystal structure in which the carbon hexagonal network faces are substantially in parallel with the axis of fibers and oriented in a coaxial manner and then  
5 bringing them into contact with fluorine.

(3) A method of manufacturing fluorinated carbon fibers as defined in claim 1, wherein the method comprises graphitizing gas phase-grown carbon fibers obtained by bringing ultra-fine metal particle catalyst suspended in a high temperature zone into contact with a hydrocarbon compound thereby obtaining  
10 graphite fibers having a three-dimensional crystal structure in which carbon hexagonal network faces are substantially in parallel with the axis of fibers and oriented in a coaxial manner and then bringing them into contact with fluorine.

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(71) Applicant: **YAZAKI CORPORATION**  
**4-28, Mita 1-chome**  
**Minato-ku Tokyo 108(JP)**

Applicant: **MITSUBISHI CORPORATION**  
**6-3, Marunouchi 2-chome**  
**Chiyoda-ku Tokyo 100(JP)**

(72) Inventor: **Endo, Morinobu**  
**615, Kitaharacho**  
**Suzaka-shi, Nagano 382(JP)**  
Inventor: **Ohashi, Yoshio**  
**4107-9, Yaho**  
**Kunitachi-shi, Tokyo 186(JP)**  
Inventor: **Katsumata, Makoto**  
**Yazaki Parts Co.,Ltd. 252, Kawashimada**  
**Gotenba-shi, Shizuoka 412(JP)**  
Inventor: **Yamanashi, Hidenori**  
**Yazaki Parts Co.,Ltd. 252, Kawashimada**  
**Gotenba-shi, Shizuoka 412(JP)**

(74) Representative: **Patentanwälte Grünecker,**  
**Kinkeldey, Stockmair & Partner**  
**Maximilianstrasse 58**  
**W-8000 München 22(DE)**

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pound, thereby obtaining graphite fibers having a three-dimensional crystal structure in which the carbon hexagonal network faces are substantially in parallel with the axis of fibers and oriented in a coaxial manner and then bringing them into contact with fluorine.

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	CHEMICAL ABSTRACTS, vol. 101, no. 16, October 1984, page 154, abstract no. 133351r, Columbus, Ohio, US; & JP-A-59 50 010 (ASAHI CHEMICAL INDUSTRY CO., LTD) 22-03-1984 " Abstract "	1	D 01 F 11/12
X	CARBON, vol. 24, no. 3, 1986, pages 343-351, Oxford, GB; T. NAKAJIMA et al.: "Preparation and electrical conductivity of fluorine-graphite fiber intercalation compound" " Whole article "	1-3	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			D 01 F
The present search report has been drawn up for all claims			
Place of search		Date of completion of search	Examiner
The Hague		25 September 91	HELLEMANS W.J.R.
<b>CATEGORY OF CITED DOCUMENTS</b>			
X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention		E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons &: member of the same patent family, corresponding document	